



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Production of Organo-Silicon Compounds

We, MONSANTO CHEMICALS LIMITED, a British Company, of 8, Waterloo Place, London, S.W.1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of silicones.

10 Silicones can be obtained by the polymerisation of organo-silicon compounds containing alkyl or aryl groups and also either halogen atoms (for instance chlorine atoms) or alkoxy groups, all directly attached to silicon.

15 This polymerisation has hitherto been carried out by hydrolysis of the monomeric organo-silicon compounds or of products already partially polymerised, 20 this hydrolysis bringing about a replacement of the halogen atoms or alkoxy groups by hydroxyl groups followed by a condensation and polymerisation with the elimination of water. Products are 25 thereby obtained in which the silicon atoms are linked together by oxygen bridges.

It has now been found that this characteristic silicone linkage can be obtained 30 by causing a molecule of an organo-silicon compound containing a chlorine or other halogen atom directly attached to silicon to react under non-hydrolysing conditions with a molecule of an organo-silicon compound containing an alkoxy or aryloxy group also directly attached to silicon, with the elimination of the alkyl or aryl halide. This reaction, therefore, affords a method of obtaining silicones 35 and by its use a polymerisation can be brought about which enables homogeneous products to be obtained. Of course, the organo-silicon molecule containing the halogen atom and the organo-silicon 40 molecule containing the alkoxy or aryloxy

group will contain such substituents as are necessary for the polymerisation to take place progressively, as will be readily understood. To give an example, if a compound containing two halogen atoms 50 is caused to react with a compound containing two alkoxy or aryloxy groups a straight chain polymer is obtained. The reaction is easier to carry out than hydrolysis, the polymerisation is progressive 55 and more uniform, and it gives less waste in the form of precipitates arising from uneven and locally excessive polymerisation. Furthermore by the choice of suitable starting materials it is possible to 60 succeed with more certainty than in previous processes in obtaining polymerisation products having the desired distribution of the different organic radicals.

The reaction is preferably carried out 65 with heating, and in the presence of a solvent and a catalyst. This latter can be chosen from the various substances which will assist the formation of the alkyl or aryl chloride, and examples are 70 ferric, zinc, calcium and aluminium chlorides. However, the reaction can if desired be carried out without a solvent, or without a catalyst.

The alkyl or aryl chloride formed can 75 be recovered and utilised.

Aluminium chloride has been found particularly valuable as catalyst, as this enables a lower reaction temperature to be used for the condensation and polymerisation, as low as 110—130° C., and a good quality silicone still to be obtained. Silicones particularly valuable for use in varnishes can be thus produced. It is of course possible to use higher temperatures 80 when using aluminium chloride, but the reaction is then more difficult to control owing to the consequent speed of the polymerisation. The advantages resulting 85 from the use of a lower temperature, and 90

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- the high quality of the products obtained when using aluminium chloride, make this a particularly valuable catalyst, even though owing to secondary reactions the quantity of alkyl or aryl chloride recovered is less than that when certain other metal chlorides are used as catalyst. There is a correspondingly increased liberation of hydrochloric acid.
- 10 The invention is illustrated by the following Examples, though it is to be understood that other pressure or temperature conditions can be employed, with or without the use of a solvent or catalyst.
- 15 It will be appreciated that in practice the process can suitably be carried out by using quantities of the reagents such that the halogen content on the one hand and the alkoxy or aryloxy content on the other 20 are approximately equinolecular, and then refluxing and distilling off the alkyl or aryl halide until the residual product is substantially free from halogen.

EXAMPLE 1.

25 170 g. of silicon tetrachloride and one litre of dry toluene were introduced into a two-litre flask provided with a reflux condenser and a stirrer, and the mixture was cooled on ice. A mixture of 335 cc. 30 of a 2.15 N. solution of an ethyl magnesium Grignard reagent in equal volumes of ether and toluene and 249 cc. of a 2.35 N. solution of a phenyl magnesium Grignard reagent in equal volumes of ether 35 and toluene were added drop by drop, after which the reaction mixture was slowly heated and refluxed for one hour. The solution of substituted chlorosilane thereby obtained was divided into two 40 equal parts, and one was placed in a two-litre flask provided with a reflux condenser and a stirrer. 57.3 g. of anhydrous methyl alcohol were slowly added, and the mixture was refluxed until the liberation of 45 hydrochloric acid ceased.

The product was then mixed with the other half of the solution of substituted chlorosilane, and 25 g. of zinc chloride in small pieces or in powder form were 50 then added. The mixture was refluxed for two to three hours and the solvent removed by distillation. The temperature rose from 80—90° C. to 220—240° C., and the operation was continued until chlorine 55 could no longer be found in the organic compounds in the liquid.

100 cc. of toluene were added to render the silicone so produced less viscous, and the catalyst was removed by several successive washings with water, which did not give rise to any hydrolysis. The solvent was then removed, leaving a pure silicone.

It was obtained as a thick oil, suitable

for instance for use in the varnish industry.

EXAMPLE 2.

Using operating conditions similar to those of Example 1, 170 g. of silicon tetrachloride were treated with 550 cc. of 70 a 3.27 N. solution of a methyl magnesium Grignard reagent in equal volumes of ether and toluene.

The substituted chlorosilane solution obtained was divided into two equal parts, 75 as above, and to one half 50 g. of anhydrous ethyl alcohol were added. It was then boiled under reflux until the liberation of hydrochloric acid ceased.

The substituted ethyl silicate so obtained was then mixed with the second half of the substituted chlorosilane solution, 25 g. of ferric chloride were added, and the operation was continued as in Example 1.

It was found that at 170° C. chlorine could no longer be found in the organic compounds in the product, and the operation was completed as described above.

After removing the more volatile components by vacuum distillation the product was a viscous oil with a very low vapour pressure, which could for example be used as a hydraulic fluid in vacuum pumps or in brakes.

EXAMPLE 3.

170 g. of silicon tetrachloride and one litre of dry toluene were placed in a flask provided with a reflux condenser and a stirrer, and a mixture of 325 cc. of a 2.35 N. solution of a phenyl magnesium Grignard reagent and 286 cc. of a 3.27 N. solution of a methyl magnesium Grignard reagent were added drop by drop, with cooling.

To 208.2 g. of cooled ethyl orthosilicate there were added drop by drop and with stirring 325 cc. of a 2.35 N. solution of a phenyl magnesium Grignard reagent and 286 cc. of a 3.27 N. solution of a 110 methyl magnesium Grignard reagent. The solvent in each case was a mixture in equal volumes of ether and toluene.

The substituted chlorosilane solution and the substituted ethoxysilane solution 115 so obtained were mixed, and 75 g. of anhydrous aluminium chloride were added.

The mixture was heated under reflux for two hours and the more volatile components were then distilled off slowly. The temperature gradually rose and after ten hours of heating reached 100—124° C. At this point, on contacting the solution with water in order to eliminate the 120 catalyst, no acid reaction was communicated to the water; thus showing the absence of unreacted chlorosilanes. Furthermore, the collected distillate con-

tained only traces of silicon compounds.
The solvent was removed, giving 216 g. of a silicone.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of 10 silicones, in which the silicone is formed by a polymerisation reaction in which the characteristic silicone linkage is obtained by causing a molecule of an organo-silicon compound containing a halogen

15 atom directly attached to silicon to react under non-hydrolysing conditions with a molecule of an organo-silicon compound containing an alkoxy or aryloxy group also directly attached to silicon, with the 20 elimination of alkyl or aryl halide.

2. A process according to Claim 1, in which the reaction is carried out under reflux.

3. A process according to Claim 1 or 25 Claim 2, in which the quantities of the halogen and of the alkoxy or aryloxy group present are approximately equimolecular, and the alkyl or aryl halide is distilled off until the residual product is 30 substantially free from halogen.

4. A process according to any one of Claims 1 to 3, in which the halogen is chlorine.

5. A process according to any one of 35 the preceding claims, in which the reaction is carried out in the presence of a solvent.

6. A process according to any one of Claims 1 to 4, in which the reaction is

carried out without the use of an ex- 40 traneous solvent.

7. A process according to any one of the preceding claims, in which a catalyst is used.

8. A process according to any one of 45 Claims 1 to 6, in which ferric chloride is used as catalyst.

9. A process according to any one of 50 Claims 1 to 6, in which zinc chloride is used as catalyst.

10. A process according to any one of 55 Claims 1 to 6, in which calcium chloride is used as catalyst.

11. A process according to any one of 60 Claims 1 to 6, in which aluminium chloride is used as catalyst.

12. A process according to any one of the preceding claims, in which a methyl-chlorosilane, a mixed methyl-phenyl-chlorosilane or a mixed ethyl-phenyl- 65 chlorosilane is used.

13. A process according to any one of the preceding claims, in which a methyl-ethoxysilane, a mixed methyl-phenyl-ethoxysilane or a mixed ethyl-phenyl- 70 methoxysilane is used.

14. A process for the production of silicones, substantially as described with reference to any one of the Examples.

15. Silicones which have been obtained 75 by the process of any one of the preceding claims.

Dated this 20th day of September, 1948.

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APPLICANT : NITTO KASEI CO LTD;

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ABSTRACT : PURPOSE: To obtain the subject reagent containing a specific ether as a solvent, capable of dissolving a halogenated magnesium complex produced as a byproduct in a coupling reaction and separating and purifying the product easily even in the case that the product is easily decomposed by water.

CONSTITUTION: This Grignard reagent of R^4MgX (R^4 is a 2-12C alkyl, an alkenyl, a 2-6C alkynyl, a 7-16C aralkyl, a 4-8C cycloalkyl or a 6-10C aryl; X is a halogen) comprises a polyalkyleneglycol dialkyl ether of the formula [R^1 , R^2 are each a 1-8C alkyl; R^3 is H or methyl; n is 1-6] (e.g. diethyleneglycol diethyl ether) as a solvent. Furthermore, it is preferable to add a hydrocarbon-based solvent such as n-hexane, cyclohexane, n-heptane, n-octane, n-decane, n-undecane, n-dodecane, benzene, toluene and xylene upon or after the preparation of the reagent.

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